TITLE: ENHANCING THE ATOMIC-LEVEL UNDERSTANDING OF CO_2 MINERAL SEQUESTRATION MECHANISMS VIA ADVANCED COMPUTATIONAL MODELING

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1. ABSTRACT

Rationale and Objective:
CO_2 mineral sequestration offers a large scale sequestration option that can provide *permanent* CO_2 disposal. Mg-rich minerals, such as brucite ($Mg(OH)_2$), olivine (e.g., forsterite: Mg_2SiO_4), and serpentine ($Mg_3Si_2O_5(OH)_4$), represent a related class of materials that are particularly well suited for this application. Among these, serpentine and olivine deposits are available in quantities sufficient to sequester a substantial fraction of the CO_2 that can be generated from all of the world's known coal reserves. Enhancing the carbonation reaction rate is the key to lowering process cost, as longer reaction times dramatically increase cost. The current project combines advanced first-principles simulation techniques with experimental observations to develop new, quantitative, atomic-level understanding of aqueous-solution serpentine carbonation mechanisms. Our atomic-level modeling studies are closely integrated with experimental work being simultaneously performed at the Albany Research Center, and in a joint Arizona State University (ASU)-Argonne National Laboratory (ANL) study that focuses on *in situ* investigations of aqueous-solution serpentine carbonation reaction mechanisms. Key focal points include (i) simulation of the morphological changes associated with serpentine heat-activation to understand its role in enhancing carbonation reactivity, (ii) development of a non-empirical site reactivity model for CO_2 with serpentine, and (iii) detailed investigation of the serpentine surface dissolution mechanisms that govern carbonation kinetics, and (iv) the use of first-principles methods to provide deeper atomic-level insight into the mechanistic experimental observations in the partner ASU/ANL studies (e.g., *in situ* studies of reaction intermediate formation).

Accomplishments Achieved During the Current Performance Period
Our study of serpentine and meta-serpentine thermal stability and decomposition during this performance period has led to new insights into dehydroxylation mechanisms leading to highly reactive feedstock materials. Significant progress has also been made in elucidating the behavior of carbon-bearing species in the aqueous reactant solution from first principles. Our modeling and simulation work also expanded to complement the increased focus by all members of the National Working Group on Mineral Sequestration on the study of carbonation in the olivine-based feedstock minerals. Our focus here has been on the quantitative description of forsterite/olivine dissolution and the properties of silica-rich passivating layers that form on feedstock grains during the carbonation process. The control/elimination of the passivation layer is currently viewed as a critical problem in the development of an efficient and cost-effective conversion process. Highlights from this performance period include:

o   Quantum molecular dynamics simulations indicate that dehydroxylation is <u>extremely complex</u>. Stable structures exhibiting staging behavior were predicted. The silica-rich sheets in serpentine minerals exhibit stability at high temperatures. First principles simulations revealed that significant proton diffusion takes place over a broad temperature range implying many paths to dehydroxylation. Simulations also identified a hitherto unknown hydroxyl conformation associated with a slightly metastable lizardite-like phase.

o   The conductor-like screening model for real systems (COSMO-RS) has been used to compute excess thermodynamic properties of CO_2-H_2O solution systems. Using quantum mechanical simulations of the solute and solvent we were

able to reproduce the exsolution behavior of H_2O-CO_2 into CO_2-rich and H_2O-rich fluid phases. Work to extend and validate the approach to 3- and 4- component fluids is ongoing.

o Solvent effects on structural and vibrational properties of carbon-bearing solutes including $CO_2(aq)$, CO_3^{2-}, HCO_3^- H_2CO_3 as well as OH^- and H_2O itself were calculated from first principles using a quantum chemical approach based on the COSMO-RS method. In addition to the structural modifications induced by solvation we calculated the shifts associated with key vibrational bands in these molecules providing important guidance for our FTIR spectroscopy studies. Our results are compatible with experiment: for water we find a downward shift of $\sim 30 cm^{-1}$ in the asymmetric stretch mode, while for CO_2 we find that solvation induces a splitting in the degenerate symmetric bend mode, just as observed experimentally. For species like HCO_3^- the situation is more complicated, and our calculations predict that solvation induced shifts can be both positive and negative. Here the largest shift ($\sim 80 cm^{-1}$) occurs in the O-C-O asymmetric stretch. Experiments are underway to verify this latter observation and provide validation for the theoretical studies so that important guidance can be generated for spectroscopic studies of the aqueous phase reactions involved in mineral carbonation.

o We studied the structure and stability of forsterite surfaces. The minimum dipole forsterite surface is predicted to be (010) while large structural reconstruction are predicted for the (100) and (001) surfaces.

o The proton exchange reaction (dissolution on (010) surface) was studied using first principles methods and predicted to be exothermic by ~ 75 kcal/mol. An analogous study of iron extraction yielded a corresponding value of ~ 55 kcal/mol suggesting that leaching leads should tend to increase the surface concentration of iron, barring unforeseen complexation reactions in the hydration layer of the reacting mineral (not taken into account in our study).

o Very large scale molecular dynamics simulations ($> 10,000$ atoms) were undertaken to study the structure and properties of the silica-rich passivating layers which form on reacting olivine surfaces. The simulations predict a low-density glass-like network with a mean density of ~ 2.0-2.2 g/cc. Furthermore, extensive "void" channels are predicted in the structure suggesting an efficient ion transport mechanisms as well a low free-energy mechanisms for the formation of secondary phases within the passivating layer matrix.

o We have systematically calculated the Si $L_{2,3}$- and O K-edge electron energy loss structure (EELS) using the structural models derived for the silica glass, and the corresponding passivation layer (PL) material. All-electron first principles quantum mechanical methods were used to compute the cross-sections. The objective is to correlate changes in the EELS edge features with local structural variations predicted by the simulations, and experiment. Our results show that the spectral differences between the glass and the crystalline EELS spectra arise from the second and third neighbor atomic shells. The oxygen K-edge spectra were found to be most diagnostic: in crystalline silica (quartz), oxygen sites are two-fold coordinated to silicon and have a fixed and narrow range of bond lengths and bond angles. In silica glass, the bond lengths and bond angles exhibit a broader distribution, and this is reflected in the EELS features. In olivine, the oxygen is coordinated to one silicon (short bond) and several magnesium ions (longer bonds), yielding a distinct EELS signature. A definitive explanation of the EELS-"local structure" correlations has emerged from a combination of first principles modeling and experimental observation. These results indicate that O K-edge energy loss spectra represent a valuable diagnostic probe of reacted material atomic structure.

2. ARTICLES, ABSTRACTS, PRESENTATIONS, AND STUDENT SUPPORT

Articles
- "Quantum simulation studies of olivine mineral carbonation". Chizmeshya, Andrew V. G.; McKelvy, Michael J.; Wolf, George H.; Kocher, Michael; Gormley, Deirdre. *Proceedings of the* 28th *International Technical Conference on Coal Utilization & Fuel Systems* **1**, 319-330 (2003).
- "Investigations of the mechanisms that govern carbon dioxide sequestration via aqueous olivine mineral carbonation". Bearat, Hamdallah; McKelvy, Michael J.; Chizmeshya, Andrew V. G.; Nunez, Ryan; Carpenter, R. W. *Proceedings of the* 28th *International Technical Conference on Coal Utilization & Fuel Systems*, **1**, 307-318 (2003).

- *"In-situ* Observation of CO_2 Sequestration Reactions using a Novel Microreaction System", G. H. Wolf, A.V.G. Chizmeshya, J.R. Diefenbacher and M.J. McKelvy, *Enviro. Sci. Tech.* **38**, 932 (2004).
- "*In Situ* Nanoscale Observations of $Mg(OH)_2$ Dehydroxylation and Rehydroxylation Mechanisms" Renu Sharma, Michael. J. McKelvy, Hamdallah Béarat, Andrew V.G. Chizmeshya, and R.W. Carpenter, *Philosophical Magazine* (In press, December 2003).

Presentations
- "Quantum simulation studies of olivine mineral carbonation", A.V.G. Chizmeshya *Proceedings of the* 28th *International Technical Conference on Coal Utilization & Fuel Systems* , March 10-13, Clearwater, Florida (2003).
- "First Principles Simulation Studies of Mineral Carbonation Reaction Processes in Serpentines", Andrew V. G. Chizmeshya, Michael J. McKelvy, George H. Wolf, Deirdre Gormley, *Second Annual Conference on Carbon Sequestration*, May 5-8, Alexandria, Virginia (2003).
- "A Study of CO2 mineral carbonation reactions in serpentine and olivine minerals using advanced computer modeling", D. Gormley, A.V.G. Chizmeshya, M. McKelvy, G. Wolf and R.W. Carpenter, Four-corner American Physical Society Meeting, October 24, Tempe, Arizona (2002).

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- Deirdre Gormley, graduate student (Ph.D.) in the Science and Engineering of Materials Graduate Program, Arizona State University.
- Michael Kocher, undergraduate research assistant (joint degree in Physics and Chemistry).